A RHEOKINETIC STUDY OF FREE RADICAL POLYMERIZATION OF POLYSTYRENE/ GRAPHITE SYSTEMS PERFORMED WITH A COUETTE RHEOMETER

A Thesis

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by

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ABSTRACT

This thesis attempts to introduce the concepts behind the research field of rheokinetics. Experiments were conducted to intensify the study of these concepts and to verify or challenge various assumptions that accompany work in this field. The experiments involved the use of a Physica Modular Compact Rheometer Model 500 to measure the viscosity of a polymer system during polymerization. All polymerizations were carried out at 85˚C. Styrene monomer and a benzoyl peroxide initiator were used in all reactions. The composition of the polymer system was varied to include either polystyrene powder and/or graphite nano-particles. The shear rate was varied as well, but for styrene → polystyrene reactions only. Both the composition and shear rate were found to have an effect on the viscosity profile of the system, especially concerning the Trommsdorff effect.

A molecular weight determination was conducted for the reacted polystyrenes. Recommendations for experimental procedural changes and future research were then made.

I. INTRODUCTION

1.1 Rheokinetics

Rheokinetics is a relatively new area of research detailing the study of the viscosity rise in polymerization reactions. The main objectives of rheokinetics research are aimed at gaining a better understanding of the kinetics of polymerization reactions and the development of a model to accurately predict the viscosity profile of the polymer during reaction (Cioffi, et al. 2004). With a better understanding of the viscosity increase associated with polymerization reactions, industrial processes could be operated more efficiently and safely than they are today. Furthermore, one of the main ideas behind rheokinetics implies that for a given reaction time, the reacting system can be used to model systems at rest of the same composition (monomer/polymer concentrations) (Cioffi, et al. 2000).

Rheokinetics most notably attempts to use the chemistry of polymerization reactions to predict the viscosity rise during reaction. In free radical polymerization reactions, as the polymer molecules react and grow, larger macromolecular groups can be formed. These groups become entangled within one another quickly as the polymer chains become larger. This development of macromolecules causes an increase in the viscosity of the system. The formation of these macromolecules is often desired in polymer materials due to higher mechanical strengths and other properties. However, the increase in viscosity is undesirable for a number of reasons. Most notably, the increase in the viscosity of the reactive system leads to problems in the development and operation of polymerization reactors.

The viscosity change that is apparent in high-conversion free radical polymerization often occurs over a relatively short time period. These rapid changes lead to problems, especially concerning the fluid dynamics within the reactor vessel or other equipment where the reaction is taking place. Presently, to avoid such complications from a rapidly changing reaction system, many polymers are often processed in the presence of a solvent. This method for production is undesirable for economic and environmental reasons. The presence of a solvent requires equipment to handle larger volumes. Also, these solvents are almost always organic chemicals which can be harmful not only to the handler, but to the environment as well.

Rheokinetics can also be used to evaluate stress relaxation time of a polymer system as well as polymer degradation (Murakami, et al. 1979). Stress relaxation has been studied in detail for many of today's most widely used polymers. Stress relaxation experiments consist of exposing a polymer sample to a specific strain and measuring the decrease of the stress on the sample with time (Billmeyer 1984). Polymer degradation has also been researched extensively. Degradation is not fully understood, but is largely a product of temperature and pressure conditions. Although these are two important phenomena to keep in mind, they are outside of the scope of this project and are not studied herein.

Rheokinetics is often studied as a function of degree of conversion of a monomer or as a function of reaction time while taking the rate constants for the reaction into account. Most current and past research divides the viscosity profile into low-viscosity (Newtonian) regions and high-viscosity (non-Newtonian) regions. The low-viscosity region corresponds to a low conversion; likewise, the high-viscosity region corresponds

to moderate to high conversions (Cioffi, et al. 2000, and Malkin, et al. 1985). In the low-conversion region, the polymer is often assumed to be Newtonian. This assumption allows for several simplifications to be made. One of the more important simplifications is the assumption that as a Newtonian fluid, the rate constants remain unchanged over the entire "Newtonian" region. This allows for the development of simplified rate expressions (Malkin et al. 1985).

1.2 Bulk Free Radical Polymerization

Free radical polymerization is widely utilized as a reaction mechanism in industrial processes. The simplified mechanism is as follows (Billmeyer, 1984):

Initiation:	$I \rightarrow 2R_1\bullet$	(1.2-1)
Propagation:	$R_n\bullet + M \rightarrow R_{n+1}$	(1.2-2)
Termination by combination:	$R_x\bullet + R_y\bullet \rightarrow R_{x+y}$	(1.2-3)
Or disproportionation:	$R_x\bullet + R_y\bullet \rightarrow R_x + R_y$	(1.2-4)

where I indicates the initiator, $R_n\bullet$ indicates a polymer chain of length n with a free radical end, M indicates the monomer, and R_n indicates a polymer chain of length n. Rate laws for these reaction steps have been derived and studied since the discovery of the importance of polymer materials. Furthermore, if rate constants are known for a polymerization reaction, the degree of polymerization can be found by analyzing a sample for composition of monomer, polymer, and initiator.

While free radical polymerization refers to the reaction mechanism, bulk polymerization refers to a reaction in which the polymer is soluble in its monomer. This

is the case with polystyrene. Excess, non-reacting styrene monomer can act as a solvent during the early stages of the polymerization, helping to keep the viscosity of the system at a relatively low value. This statement is supported in the equations illustrating the reaction mechanisms (equations 1.2-1 thru 1.2-4) when the size and molecular weights of each component in the reaction are considered.

1.3 Shear Viscosity

Viscosity may very well be the most important property of a polymer. The viscosity of a polymer system must be understood in order to create a successful and efficient process. Because of this, the viscosity of polymer systems has been widely researched. Numerous models have even been suggested for the prediction of the viscosity dependence on stress and/or shear rate. However, these models rarely, if ever, take into effect any additives to the polymer system.

Polymer composite materials are becoming more important in industrial and research applications. In recent research, these composite materials often use nano-particles such as nano-clay or talc to increase the viscosity of the polymer for various reasons. The effects of these particles are discussed more thoroughly in section 1.4.

The viscosity of any fluid is dependent on the stress and the shear rate. As such, when testing the viscosity of a system, the test is often performed either for controlled stress with measured shear rate or controlled shear rate with measured stress. Shear viscosity refers to the collection of viscosity data under controlled shear rate conditions. In a shear viscosity experiment, the shear rate of the system is controlled and the stress is measured often by measuring the torque on the screw. It is also possible with some

equipment to control the shear rate and measure the normal forces exerted by the polymer on the equipment. Using the stress and shear rate values, the viscosity can be determined with one of the numerous models (including Newton's Law of Viscosity) for either the entire curve or simply point-by-point. Calculations are simplified for Newtonian assumptions, as Newton's Law of Viscosity can be used. Newtonian behavior can be characterized by equation 1.3-1:

$$\tau_{xy} = -\eta\gamma \tag{1.3-1}$$

where τ_{xy} is the shearing stress, η is the viscosity, and γ is the shear rate.

There are two major types of instruments used in collecting viscosity profile data for a given fluid: capillary and rotational rheometers (Brodkey 1967). Rotational rheometers are of primary interest in polymer applications and research. This is largely due to the high viscosity of polymeric materials and their inability to easily undergo capillary flow. Of the many rotational devices available today, two of the most widely used are parallel plate rheometers and couette rheometers.

Parallel plate rheometers consist of two parallel plates; one plate is rotated at a specified rate to allow the sample to undergo the desired shear while the other plate remains stationary. The machine often collects measurements of the normal forces and torque in order to determine the viscosity of the sample. One popular variation of the parallel plate rheometer is the cone and plate rheometer. The same principles apply to this geometry as the parallel plates, but the top plate is replaced with a cone.

Couette rheometers consist of a couette cup with a bob that rotates inside. Ideally, the inner diameter of the couette and the outer diameter of the bob would be very similar as to create a narrow region between the wall of the couette and the bob. This narrow

region would impose laminar flow of the sample, and Newtonian behavior could be assumed. The viscosity measurements would reflect the flow of the polymer or other material within this narrow region.

1.4 Use of Graphite Nano-Particles

In recent years, the addition of nano-particles to polymer melts has become increasingly important in research as well as industry. Recent research done in the Department of Chemical and Biomolecular Engineering at The Ohio State University has studied the use of talc and nano-clay as additives to polymer systems. These nano-particles have been found to impose an increase on the viscosity of the polymer melt. In foaming processes, these nano-particles serve as nucleating agents. Graphite particles are of particular interest because they are environmentally benign with unique qualities.

There are many purposes to using nano-particles in polymer systems. One such purpose is to increase mechanical properties of the polymer via uniform dispersion of the nano-particles during in-situ polymerization (Zeng, et al. 2003). In addition to improved mechanical properties, it is believed that uniform dispersion of nano-particles in polymer foams can provide better thermal insulating properties. Most importantly, nano-particles may help decrease the diffusion of CO_2 out of polymer systems when CO_2 is used as either a blowing agent in a foaming process or as a solvent.

Nano-graphite particles have not yet been studied extensively in polymer research, but the addition of nano-graphite is believed to have desirable effects. The structure of nano-graphite is similar to that of nano-clay that has been studied recently in other research. It is believed that the addition of nano-graphite platelets will facilitate

foaming processes by creating cell nucleation sites in addition to decreasing gas diffusion out of the melt (Chung 1987). Furthermore, graphite may act as an infrared attenuation agent, improving the thermal insulation qualities of composite foams. It is important to note that nano-graphite polymers are more economical to use and produce than nano-clay materials.

1.5 Literature Review

The Trommsdorff effect refers to the phenomenon of non-linear autoacceleration in bulk free radical polymerization. Cioffi, et al. have studied the Trommsdorff effect through rheokinetic experiments. The focus of their research was to reduce the Trommsdorff effect as to make industrial processes more efficient. The bulk free radical polymerization of styrene and n-butylmethacrylate was initiated with peroxide in the study. Viscosity measurements were taken using a self-constructed helical barrel rheometer with intent to model reactive extrusion processes. The results of the rheokinetic study performed by Cioffi, et al. indicate that the Trommsdorff effect can be significantly reduced or even eliminated by operating at a higher average shear rate.

Malkin et al. elaborated on theoretical kinetic concepts of free radical polymerization to explain the increase in viscosity of a reacting polymer system. The authors describe the viscosity increase as determined by the increase of the molecular weight of the polymer and the amount of high molecular weight polymer in the system. Through theory and equations, it is shown that the change in viscosity can be determined if time or conversion is taken to be an independent variable. Malkin et al. use equation 1.5-1 to show this.

$$\eta = K\beta\left(\frac{[M]_0\beta}{[I]_0(1-e^{-k_i t})}\right)^a \qquad (1.5\text{-}1)$$

In equation 1.5-1, η is the viscosity of the system, β is the degree of conversion, k_i is the rate constant of initiation, $[M]_0$ and $[I]_0$ are the concentrations of monomer and initiator, respectively, and K, a, and b are constants.

Malkin et al. used a series of alkyl methacrylates and styrene with a benzoyl peroxide initiator to study rheokinetics. The research focused on the effects of initial concentration of initiator, reaction temperature, and time on the viscosity of the polymer system. Unlike Cioffi et al. whose research focused on high-conversion polymerizations, Malkin et al. focused their research on low to moderate-conversion reactions. This was controlled in order to assume that the rate constants for a given reaction remained constant. They were able to conclude that the viscosity rise at the initial stages of reaction could be predicted as a function of initial concentration of initiator and temperature. However, Malkin, et al. did not study the dependence of viscosity on shear rate.

González-Romero and Macosko studied the viscosity rise of a styrene-dimethacrylate (SDM) system in an isothermal environment. The research used a cone and plate rheometer with an environmental chamber to control temperature. One focus of the research was to observe any dependency of the viscosity rise on the gel point. The authors were able to suggest an expression for the gel time that was dependent on kinetic data for their system.

1.6 Purpose

The goals of the research are to gain a basic understanding of rheokinetics by the characterization of the polymerization of styrene. The research aims to compare rheokinetic data for polystyrene systems with and without nano-graphite particles as an additive as well as compare the polymerization of the styrene monomer at different rotational speeds (shear rates) of the screw. The purposes of the research are to examine the effects of nano-graphite particles on the viscosity of the polymer as it reacts and to determine the extent of the Trommsdorff effect for the extent of reaction for which the viscosity values are obtained. Additionally, the validity of the Newtonian assumption will be examined for low-viscosity regions. Furthermore, the molecular weight will be noted for each reaction producing pure polystyrene in an attempt to determine whether the equipment used is suitable for creating reproducible polymerization results.

II. EXPERIMENTAL

2.1 Materials

All experiments focused on the polymerization of a styrene monomer with a benzoyl peroxide, 97% (BPO) initiator. The styrene was purchased from Mallinckrodt Chemicals and the BPO was purchased as Luperox® A98 from Aldrich Chemicals. In two of the experiments, a polystyrene (PS) powder was first dissolved in the monomer in order to increase the viscosity to allow for uniform dispersion of the graphite particles. The PS powder was purchased from NOVA Chemicals. The graphite particles used were milled expanded graphite worms from Superior Graphite Co. All materials were used without further purification. Also, tetrahydrofuran (THF) and acetone were used extensively for cleaning. Both of these chemicals were from Mallinckrodt Chemicals.

2.2 Rheometer Setup and Procedure

2.2.1 Couette Geometry

A Physica (an Anton Paar Company) Modular Compact Rheometer (MCR) Model 500 was used to perform all rheokinetic experiments. While running a polymerization reaction, it is important to have good mixing throughout the system in order to obtain a reasonably uniform temperature profile as well as a reasonably uniform reaction within the vessel. For this reason, a couette geometry was used with the MCR 500 for all rheokinetic studies. The approximate dimensions of the couette and bob can be seen in Figure 1.

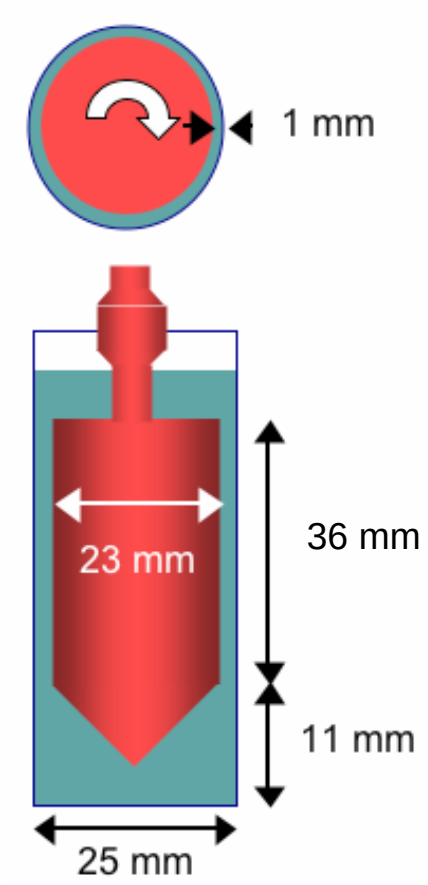

Figure 1: MCR 500 Couette and Bob Dimensions

The bob is driven by a magnetic force to rotate at a specified rate. The viscosity of the material inside the couette is calculated from a torque signal transmitted from the machine to the software. In order for the viscosity to be calculated, the torque signal must be above some minimum value. This means that the couette geometry must only be used for materials or systems of relatively high viscosity.

The couette geometry was used along with a special high-pressure attachment. Although this pressure cap was originally developed and used by researchers at The Ohio State University to test the viscosity of polymer systems in the presence of high-pressure gas, the pressure cell allowed for a way to prevent the styrene monomer from evaporating

to the atmosphere before it was reacted to form PS. Figure 2 shows an image of this high-pressure cell.

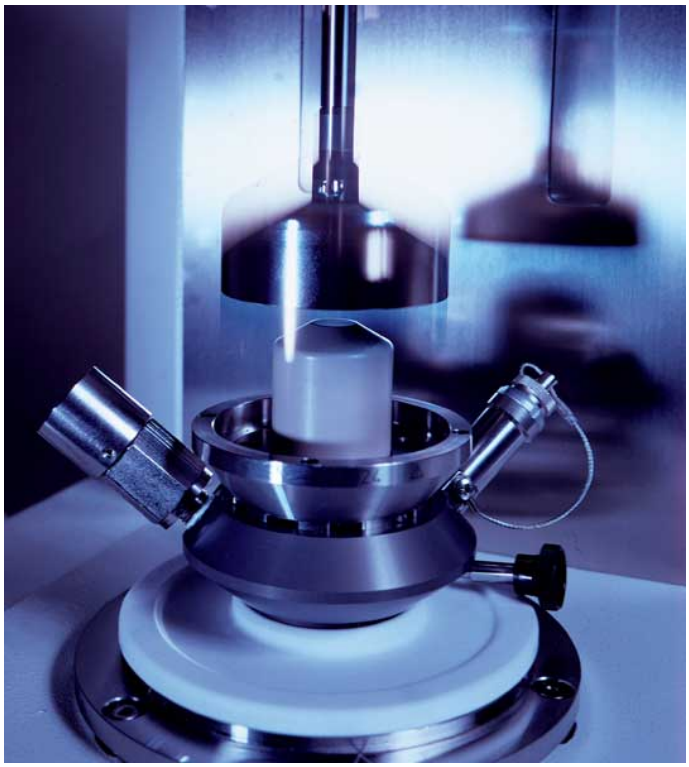

Figure 2: Pressure Cell for MCR 500 (from http://www.anton-paar.com/)

The first step in conducting any of the rheokinetic studies for this thesis was to turn on both the temperature controller and the MCR 500. Once the system was powered on, the accompanying software could be used to start the experiment. Before each run, it was important to remember to first initialize the system and to set the normal force measurement to zero. This was done with an empty couette in the system. Before every other experiment, the system was calibrated by running a motor adjustment and air test. The system was assumed to be running as expected if the air test produced torque values within a ±100 unit range.

For each polymerization conducted, the sample was first weighed out and prepared according to desired composition. The sample was stirred with a spatula to be sure that all solid particles had been dissolved in the styrene monomer. The sample preparation was done in the couette that would be used for the experiment. The couette was then placed inside the rheometer. The bob and cap to the high-pressure cell were then tightened down on the sample. The system was then heated to the desired temperature. In these experiments, the temperature for reaction was held constant across all experiments at 85˚C. Once the temperature had reached about 80˚C, the test could be started with the software.

Each experiment took between two and three hours to complete. The experiment was over when the upper torque limit was exceeded because of the high viscosity of the polymer. Because it is much safer to dispose of a polymer than a monomer, the system was maintained at 85˚C overnight. Sometime between 20-24 hours later, the sample would be heated up to 120˚C for 2 hours, then 160˚C for one hour, and finally 180˚C for 30 minutes. This step constituted a post-cure for the polymer.

Upon completion of the post-cure, the pressure cap and the bob would be removed from the system and set aside. A bronze rod was then used to collect polymer sample from the couette. Additional polymer was collected from the bob after it cooled by simply cracking or peeling it off.

For cleaning, the entire system was soaked in THF for up to 48 hours. Usually, the cleaning process took anywhere from 12 to 24 hours but occasionally a large mass of polymer would remain uncollected in the couette, thus making cleaning more time consuming. After being removed from the THF, the system was wiped down with

acetone. It is important to note that the threads connected the pieces of the high-pressure cell were particularly important to clean. They were wiped with a baby wipe after being removed from the THF and then sprayed with acetone.

Each rheokinetic experiment took approximately two days to complete. The polymer samples created were saved for a molecular weight analysis of the polymer.

2.2.2 Parallel Plate Geometry

To test the viscosity of the polymer samples collected after the rheokinetic study, the MCR 500 was setup with a parallel plate geometry. The plates used were 25 mm in diameter: model PP 25 (4133). In order to maintain the temperature, the Convection Temperature Device (CTD) Model 600 was used in conjunction with the parallel plates. A picture of the setup can be found in Figure 3.

The procedure for the CTD 600 and PP 25 began with turning on the equipment as well as the air-cooling stream to the CTD 600. The system was initialized via the software. The top plate was then inserted into the coupling on the MCR 500. At this time, the measuring gap could be zeroed and the specifications for the test, including temperature, angular frequency, and lift position, could all be set.

Figure 3: Parallel Plates with CTD 600 (from http://www.anton-paar.com/)

Once the temperature reached 180˚C, the polymer sample could be loaded. Normally, the polymer samples would first be compression molded before being tested in the parallel plates. However, because it was so difficult to collect the final polymer, in this experiment the sample was placed directly onto the lower plate. The polymer was watched very closely. As it melted, the top plate was lowered so that it would remain in contact with the melt. The polymer was trimmed with a razor blade as necessary. The final gap for measurement was desired to be approximately 0.60 mm. The final trim of the polymer was completed when the gap was at 0.63 mm or 105% of the final value. The temperature was allowed to stabilize before beginning the test.

It is important to note that degradation of the polymer could pose a problem at 180˚C. For this reason, the thermal history of each sample was recorded. It was

attempted to maintain each sample at 180˚C for the same amount of time. This would significantly reduce, if not eliminate any differences in viscosity due to degradation. Each test took approximately 45 minutes, including cleaning time.

2.3 Methods

The MCR 500 can be used for a variety of test conditions. The maximum torque limit is around 120,000 μNm. The rheometer can perform both steady shear rate and steady stress tests to determine viscosity. This was important for running the rheokinetic experiments. All rheokinetic studies were completed via constant shear rate experiments. In these experiments, the rotational rate of the screw (i.e. the shear rate) was specified as 0.5, 1, or 5 rpm.

For the parallel plate experiments, an oscillatory mode was used. In this test mode, the angular frequency, ω, was specified. For the experiments performed in this study, the angular frequency was varied from 0.1 to 10 s^{-1}.

III. RESULTS AND DISCUSSION

3.1 General Characterization

The experiments conducted can be summarized in terms of shear rate and composition. This information can be found below in Table 1. The initial amount of BPO added as initiator was 1 wt% for all reactions. The data from 1/12/05 was provided courtesy of Max Wingert and Jiong Shen.

Table 1: Summary of Experimental Trials

Date	PS Powder (wt%)	Graphite (wt%)	Rotational Rate (rpm)	Shear Rate (1/s)
1/12/05	0	0	1	1.2854875
3/7/05	0	0	1	1.2854875
3/18/05	0	0	5	6.4274375
3/20/05	0	0	0.5	0.64274375
5/2/05	10	0	1	1.2854875
5/5/05	10	0.25	0.5	0.64274375

As expected, the viscosity increased with time for each rheokinetic study. This can be seen in Figure 4. From this figure however, it is unapparent as to whether or not the composition or shear rate has any effect directly on the viscosity profile during reaction. It is noticeable that the maximum torque limit was not exceeded as quickly for those experiments involving lower shear rates as those involving higher shear rates. At the end of each curve, there are also data points that seem to be obviously out of place. These data points were collected while the torque limit was being exceeded. The plot of these experimental values can be seen without these points in Figure 5.

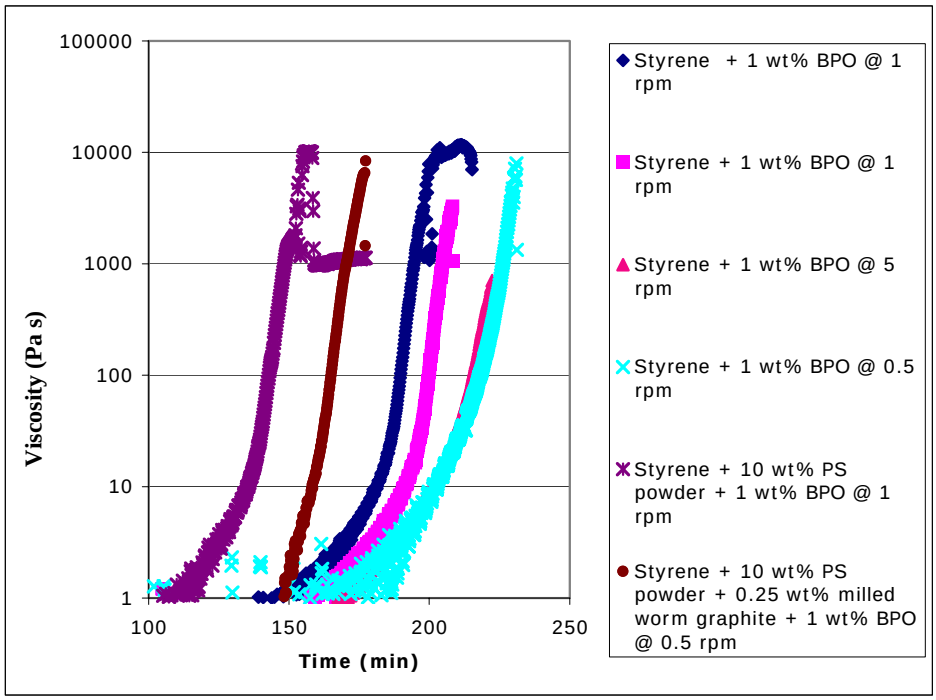

Figure 4: Raw Data for All Rheokinetic Experiments

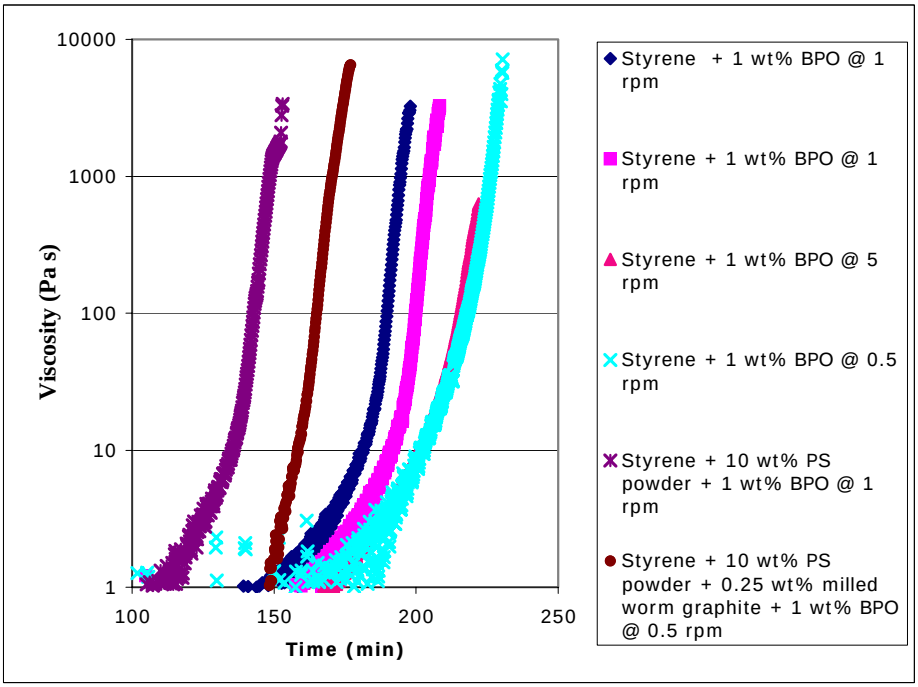

Figure 5: Corrected Data for All Rheokinetic Experiments for Torque Limit

Because no conclusive results could be determined from Figure 3.2, each trial was plotted separately and fit to a power law in order to determine the effects of composition and shear rate on the viscosity profile (see Figures 6-11). The data for each curve was then fit to two power law curves of the form (Cioffi, et al. 2004)

$$\eta = at^b \tag{3.1-1}$$

where η is the viscosity, t is time, and a and b are constants.

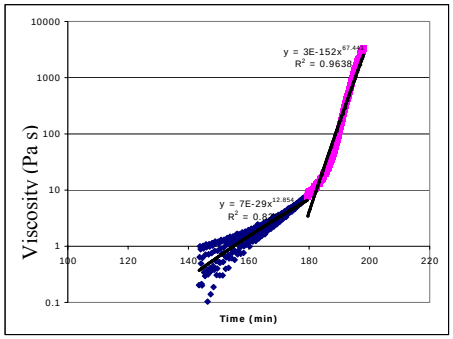

Figure 6: Viscosity v. Time for the Reaction of Styrene + 1 wt% BPO @ 1 rpm

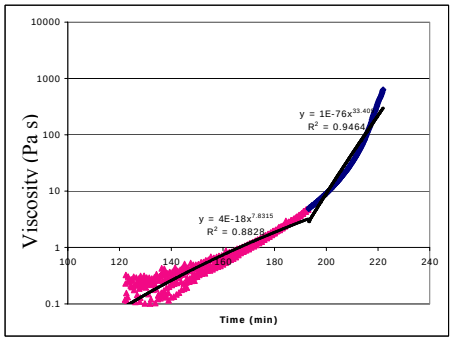

Figure 7: Viscosity v. Time for the Reaction Styrene + 1 wt% BPO @ 5 rpm

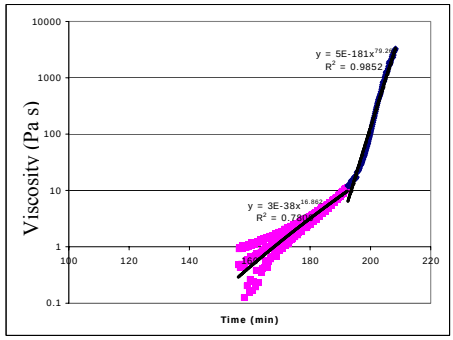

Figure 8: Viscosity v. Time for the Reaction of Styrene + 1 wt% BPO @ 1 rpm

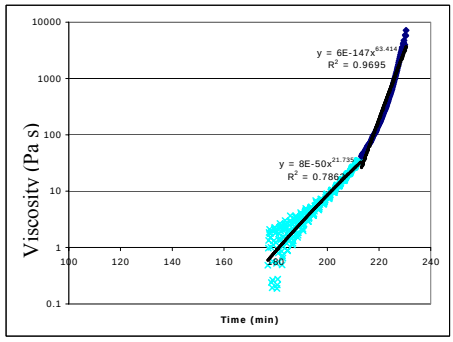

Figure 9: Viscosity v. Time for the Reaction of Styrene + 1 wt% BPO @ 0.5 rpm

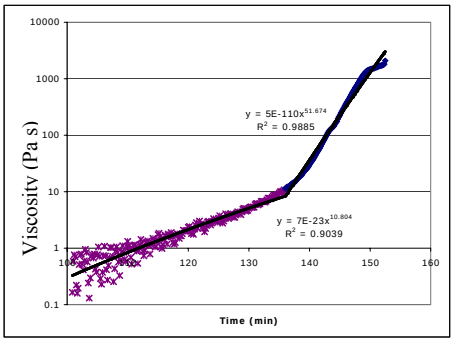

Figure 10: Viscosity v. Time for the Reaction of Styrene + 1 wt% BPO + 10 wt% PS powder @ 1 rpm

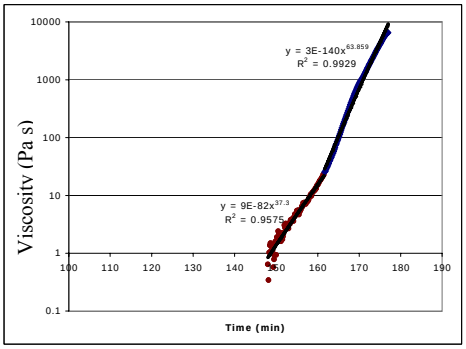

Figure 11: Viscosity v. Time for the Reaction of Styrene + 1 wt% BPO + 10 wt% PS powder + 0.25 wt% Graphite @ 0.5 rpm

From each of these plots, the power law expressions can be compiled as seen in Table 2. It is important to note that although the error margin for the trend line fit for the lower region of each curve is significant, this is largely due to the fact that the viscosity values are unstable until a minimum torque value is reached; it is not because the trend line is a poor fit.

Table 2: Power Law Data for Each Curve

Trial (Figure #)	Lower Curve			Upper Curve		
	a	b	R^2	a	b	R^2
6	7E-29	12.854	0.8287	3E-152	67.441	0.9638
7	4E-18	7.8315	0.8828	1E-76	33.409	0.9464
8	3E-38	16.862	0.7809	5E-181	79.26	0.9852
9	8E-50	21.735	0.7862	6E-147	63.414	0.9695
10	7E-23	10.804	0.9039	5E-110	51.674	0.9885
11	9E-8	37.300	0.9575	3E-140	63.859	0.9929

3.2 Non-Newtonian Behavior

Some of the literature that was reviewed assumes that at low viscosities, the polymer systems behave like a Newtonian fluid. This assumption is an important one to test. The measured viscosity values for each trial were compared to viscosity values calculated using the measured stress and the shear rate, which was specified for each experiment. Relative errors were calculated. For the purposes of this thesis, any error less than 10% supports the assumption that the polymer is a Newtonian fluid at low viscosities.

As a general observation, the graphite/polymer system showed no Newtonian behavior even at low viscosities. It should be noted that a polymer solution containing styrene, 10 wt% PS powder, 1 wt% BPO, and 1 wt% graphite was tested as well. However, this test could not be completed. The solution was much too viscous before reacting, and the equipment could not measure the torque.

For the values obtained by experimental measurements, the Newtonian assumption cannot be fully investigated. A plot of stress versus shear rate is given as a linear relationship for a Newtonian fluid. This direct proportionality is the viscosity of the fluid; because the viscosity of the systems of interest is always changing with time (i.e. conversion), a standard stress versus shear rate curve cannot be created. In order to fully challenge the assumption that the system is Newtonian, data must be collected over a wide range of shear rates for a variety of times. Therefore, at any given time, the stress versus shear rate curve could be obtained. However, it is interesting to note that the measured and calculated viscosity values are not equal.

3.3 Trommsdorff (Gel) Effect

From the graphical data (Figures 6-11) in conjunction with the power law fit (Table 2), it can be seen that the viscosity of the graphite/polymer mixture climbed the faster at the beginning of the reaction than in any other system. This is supported by the high value for *b* in the power law expression for the lower-viscosity curve of 37.300. The other exponents are significantly lower. The second highest exponent *b* comes from the trial involving the polymerization of styrene at 0.5 rpm. Again, the value of 21.735 is significantly higher than any of the data from the styrene → PS reactions. This supports Cioffi, et al.'s findings that the Trommsdorff effect may be reduced at higher shear rates. That theory is further supported by the fact that the reaction of styrene → PS at 5 rpm has the lowest valued exponent of all the reactions.

As described by Cioffi, et al., the Trommsdorff effect occurs for values of $b \gg 7$. Under this assumption, all of the high-viscosity regions seem to be experiencing the effect to some degree. For the trial previously mentioned as having the lowest *b* value for the lower end of the curve (styrene → PS @ 5 rpm), the exponent for the high-viscosity curve is also significantly less than those for the other reactions. It is described by Cioffi, et al. that the Trommsdorff effect can be measured by considering the difference between the lower and upper curves' exponential values. This effective measurement can be seen in Table 3 for the experimental data. It is proven here that the highest rotational rate yields a reduced gel effect while the lowest rotational rate yields the highest value.

Table 3: Trommsdorff Effect Measurement - Difference between upper and lower curve *b* values

Trial (Figure #)	Trommsdorff Measure
6	54.587
7	25.5775
8	62.398
9	41.679
10	40.87
11	26.559

It is interesting to notice that the gel effect is not significantly larger for the reaction involving graphite particles than that of the reaction at 5 rpm. More studies should be completed to determine how the gel effect depends on particle concentration within the system. At this time, it seems that the addition of a small amount of nano-particle (0.25 wt% graphite) can reduce the Trommsdorff effect comparable to the reduction due to increased shear.

3.4 Molecular Weight Analysis

In order to determine that the couette vessel was suitable for reaction and to verify that the current procedure including post-cure allowed for the polymer to be fully formed, a molecular weight determination was completed. The viscosity data in Figure 12 was collected using the parallel plates. The average molecular weight (see Table 4) was found using the following equation (Billmeyer, 1984):

$$\eta = K M_w^{\,a} \qquad (3.4\text{-}1)$$

with $K = 3.4$ and $a = ½$ for polystyrene.

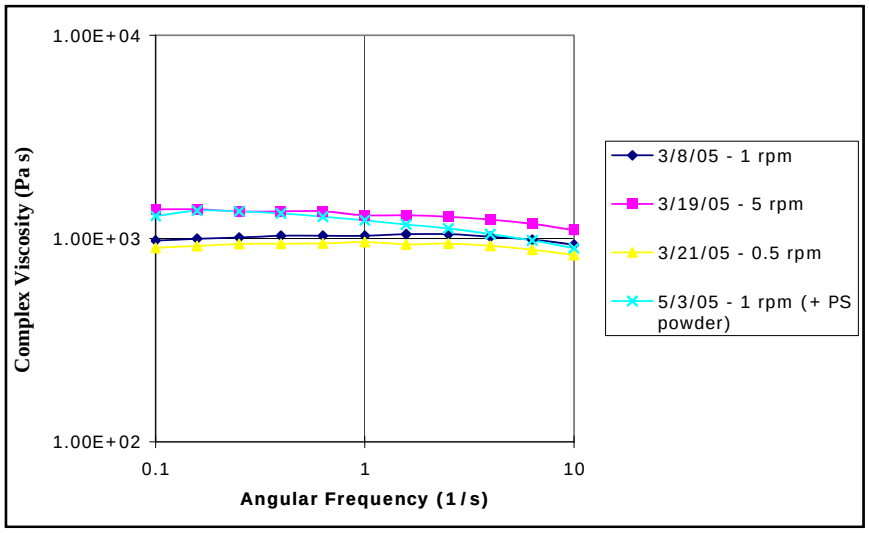

Figure 12: Viscosity Data for PS Only Polymers Created During Rheokinetic Experiments

Table 4: Molecular Weight Determined From Viscosity Data

Trial	$M_{W,AVG}$
3/8/05 - 1 rpm	88327.69
3/19/05 - 5 rpm	146047.5
3/21/05 - 0.5 rpm	73213.26
5/3/05 - 1 rpm (w/PS powder)	124206.6

These results are interesting to note, as there is a significant difference in the average molecular weight for the polystyrene formed as a result of four different reaction conditions. These differences may be due to shear rate differences, but it cannot be concluded from this data. Further studies should be conducted.

It is important to note also that this determination of molecular weight is valid for pure polymers only; therefore the trial involving graphite particles could not be involved in this study.

IV. CONCLUSIONS

The viscosities of all systems increased exponentially with time. When each experimental viscosity profile was split into a lower and upper viscosity region, a simple power law fit the data relatively well. Upon examination of the constants accompanying each power law trend line, it could be determined that the gel effect was reduced for the reaction occurring at the highest rotational speed of 5 rpm. Furthermore, it was determined that the incorporation of the graphite nano-particles into the polymer system during reaction not only increased the viscosity more rapidly than polymer alone. The inclusion of graphite also may have the added effect of reducing the gel effect. This should be investigated more thoroughly.

The assumption that the polymer systems behave as Newtonian fluids was challenged and found to be invalid for the systems of interest in this research. Additionally, the molecular weight of the polymer collected after each rheokinetic study was found. It can be hypothesized that the rotational (shear) rate imposed on the system by the rheometer plays a role in the conversion of the monomer to polymer and on the molecular weight of the polymer that is formed.

V. RECOMMENDATIONS

5.1 Experimental Changes

5.1.1 Rheokinetic Study

There are several changes that could be made to the current experimental protocol for the rheokinetic studies that took place as part of this research. First and foremost, it would be encouraged to collect more data by performing more experiments. Many of the polymer systems of interest in this research were only studied during one polymerization. More reactions and studies would be advised in order to gain a better understanding of the viscosity characteristics of each polymer system.

Because all reactions accompanying this research were performed isothermally, it is important to know that the temperature control mechanism for the vessel works properly. For this reason, it is advisable that a temperature probe be developed that is able to detect the temperature inside the vessel. If this were accomplished, it could be determined whether or not the process was taking place isothermally or not.

Finally, in regards to preparation of the initial system (i.e. monomer and initiator with any additives), some type of stirring system should be developed to help insure that any solid particles are uniformly distributed throughout the system. It might be useful here to conduct a separate, smaller study simply stirring a system for varying amounts of time and testing the initial viscosity only to see how stirring affects the system. Furthermore, it should be investigated as to how much time is required for the PS powder particles to become completely dissolved in the styrene monomer. It would also be helpful to determine how much time can pass without the evaporation of styrene into the

atmosphere. Based on these determinations, a sample could be prepared in advance for a rheokinetic study.

5.1.2 Molecular Weight Analysis

For the molecular weight analysis involving the parallel plate geometry, there may have been air bubbles trapped inside the sample during testing due to the method used for melting the polymer. To avoid this, it would be useful to make compression-molded discs for samples. In order to have enough sample for compression molding, sample should be collected very carefully when the rheokinetic study is complete. To facilitate polymer collection, it might be helpful to expose the polymer to higher temperatures than 180C for a short time period or even expose the sample to 180C for a longer period of time. Degradation studies would be important in determining how long the sample could be exposed to harsh conditions before breaking down. It also may be useful to seal the high-pressure cap tightly while heating during post-cure in order to reduce oxidation.

5.2 Future Research

In conducting this research, several opportunities for further study have become apparent. The most obvious subject for future work would be to further investigate the effects of nano-particles on the system. This study could involve different types of nano-particles or simply different concentrations of one nano-particle. It would also be useful

to study the dispersion of nano-particles within the polymer system as a function of the concentration of PS powder added.

Another useful study comes from an extensive literature review. Several of the researchers cited in this thesis studied the Trommsdorff or gel effect (Cioffi, et al. 2000, 2004, Malkin et al. 1985). It would be useful to perform more studies in order to better characterize the Trommsdorff effect for each polymer system. These experiments should be run at varying rotational rates (shear rates) in order to determine the extent of the gel effect with rotation rate. It might also be useful to study the gel effect as a function of composition (i.e. wt% nano-particles).

It might also be useful to perform a study to determine the Arrhenius effect on viscosity. This could be achieved by running the experiment under non-isothermal conditions and allowing the temperature to change due to the extent of the reaction. It might also be helpful to try to run the polymerization at different temperatures isothermally to determine temperature effects.

Another simple study might be to vary the initial concentration of initiator in the system and determine how that affects the viscosity of the polymerization. It was suggested by Cioffi, et al. that the initial concentration of initiator might play a role in the increase of the viscosity. Perhaps a greater amount of initiator would cause a greater increase in viscosity at a shorter reaction time.

A solvent study would be useful as well, as solvents are used extensively in industrial polymer process operations. Possible solvents might be organic compounds or supercritical fluids such as CO_2. This study would be useful in determining if a solvent

could reduce the gel effect, the overall viscosity, or the Arrhenius effect when used in conjunction with suggestions mentioned prior.

Finally, in order to characterize a reaction mechanism for the polymerization, it would be useful to have some way of determining the composition of monomer, polymer chain, and initiator in the system. This type of study could allow each experiment to run for the same set amount of time. At that time, the reaction could be stopped with an inhibitor that was added either at the beginning or at a given time. The solution could then be tested for composition via NMR or some other method. The degree of conversion of the monomer could then be determined and a rate law could be suggested for that system following Malkin, et al.'s approach to a viscosity-related rate law (see equation 1.5-1). The study could focus on working a shear rate dependency into Malkin, et al.'s formula.

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